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TRIPLY-BRIDGED DIBORON SPECIES OF THE PYRAZABOLE TYPE
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Triply-Bridged Diboron Species of the Pyrazabole Type

by

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J. Bielawski and K. Niedenzu

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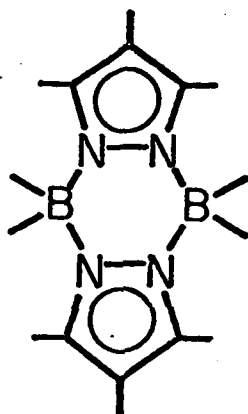
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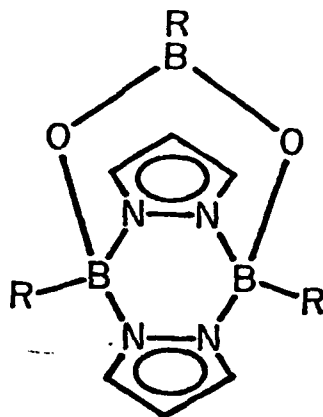
Introduction

The pyrazaboles = dimeric pyrazol-1-ylboranes (1) are a chemically remarkably stable class of heterocycles containing four-coordinate boron.² Although various boron- and/or carbon-substituted derivatives are known, so far no species containing boron-bonded OH or alkoxy groups have been described. As a matter of fact, the only known pyrazaboles containing B-O bonds are one phenol³ and two catechol^{3,4} derivatives.



1

In our search for B-O derivatives of pyrazaboles, we have accidentally obtained a novel type of pyrazabole, in which the two pyrazabole-boron atoms are also bridged by a O-BR-O group. Thus, the species contain not only two four-coordinate but an additional three-coordinate boron as shown in 2.



2

Dibora-monocations of the type $[\text{RB}(\mu\text{-pz})_3\text{BR}]^+$, in which the boron atoms are bridged by three pyrazolyl groups, are structurally related to species of type 2. Only two examples of the former have so far been described in the literature.^{5,6} Within the framework of the present investigation on diboron species containing the unit $\text{B}(\mu\text{-pz})_2\text{B}$, the specific preparation of $[\text{RB}(\mu\text{-pz})_3\text{BR}]^+$ ions has also been studied. Such species were obtained from either pz^- or $[\text{RB}(\text{pz})_3]^-$ by reaction with trigonal boranes containing two readily leaving groups X, i.e., R^-BX_2 .

The present investigation is supplemented by some studies on B- and/or C-substituted pyrazaboles. They include the preparation and characterization of $(\text{C}_2\text{H}_5)_2\text{B}(\mu\text{-pz})_2\text{B}(\text{C}_6\text{H}_5)_2$, the first known pyrazabole containing two different hydrocarbon substituents on the two boron atoms.

Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY; all compounds gave satisfactory data. Melting points (uncorrected) were determined on a Mel-Temp block. NMR spectra were recorded on a Varian XL-200 instrument. Chemical shift data are given in ppm with positive values indicating downfield from the reference (internal Me_4Si for ^1H and ^{13}C , external Et_2OBF_3 for ^{11}B); s = singlet, d = doublet, t = triplet, q = quartet, m = unresolved multiplet and an asterisk denotes a broad signal. Coupling constants J are given in Hz. Infrared spectra were recorded on a Perkin-Elmer Model 621 instrument under standard operating conditions; w = weak, m = medium, s = strong, v = very, br = broad, sh = shoulder.

$\text{C}_2\text{H}_5\text{B}(\mu\text{-pz})_2(\mu\text{-OBC}_2\text{H}_5\text{O})\text{BC}_2\text{H}_5$ (2, R = C_2H_5). A mixture of 19.0 g (113 mmol) of B-triethylboroxine and 23.15 g (340 mmol) of pyrazole was slowly warmed to give a clear solution that was refluxed for 6 h. On cooling to room temperature, a pasty material remained which was treated with 80 mL of water. The colorless insoluble material was collected and dried in vacuum over P_4O_{10} to give 25.8 g (90%) of crude product. The latter was recrystallized from cyclohexane to give 20.2 g of pure material, mp 126-128°C.

NMR data (solution in CDCl_3): δ (^1H) = 7.71 (4 H, d, J = 2.4), 6.28 (2 H, t, J = 2.4), 1.15-0.56 (15 H, m); δ (^{11}B) = +31.5 (1 B, s, $h_{1/2}$ = 600 Hz), +1.8 (2 B, s, $h_{1/2}$ = 140 Hz); δ (^{13}C) (proton decoupled) = 133.9, 104.7, 8.7, 8.5. (Note: The intensity of the last two signals is 2:1; the boron-bonded carbon atoms were not observed but were indicated by a very broad signal underneath those of the CH_3 groups.)

Infrared spectrum (KBr pellet): 3160 (sh, vw), 3130 (w), 2970 (s), 2900 (s), 2850 (w,sh), 1510 (m), 1455 (w-m, sh), 1418 (s), 1320 (vs, br), 1290 (s,

sh), 1199 (vs, br), 1128 (w), 1070 (s, br), 1020 (m, br), 985 (w, sh), 875 (w, sh), 815 (m-s, br), 752 (s, br), 615 (m, vbr).

$C_6H_5B(\mu-pz)_2(\mu-OBC_6H_5O)BC_6H_5$ (2, R = C_6H_5). A solution of 6.2 g (20 mmol) of B-triphenylboroxine and 5.4 g (80 mmol) of pyrazole in 50 mL of bromoform was refluxed with stirring for 7 h. After cooling to room temperature, a very small amount of insoluble material was filtered off and the clear solution was washed with 100 mL water, dried and the solvent was removed under vacuum to leave 7.1 g (83%) of crude product. The latter was purified by recrystallization from cyclohexane to give a pure compound, mp 202-204°C.

NMR data (solution in $CDCl_3$): $\delta(^1H) = 8.17$ (2 H, m), 7.97 (4 H, m), 7.49 (m) + 7.36 (m) (13 H), 6.10 (2 H, t); $\delta(^{11}B) = +28.7$ (1 B, s, $h_{1/2} = 800$ Hz), +1.5 (2 B, s, $h_{1/2} = 290$ Hz).

$[C_2H_5B(\mu-pz)_3BC_2H_5]^+[PF_6]^-$. A slurry of 3.19 g (30 mmol) of potassium pyrazolide in a solution of 7.6 g (20 mmol) of ethylboryl ditosylate⁵ in toluene was refluxed with stirring for several h. After cooling to room temperature, 40 mL water was added and the mixture was stirred at ambient temperature for 1 h. The aqueous layer was separated and 2.5 g (15 mmol) of ammonium hexafluorophosphate were added with stirring. The resultant insoluble material was collected, washed with water and then ether and was dried to give 0.95 g (22.3%) of crude material. An analytical sample, mp 298-302°C (lit.:⁵ mp 299-301°C), was obtained by dissolving the compound in acetone and precipitation with diethyl ether, and subsequent recrystallization from acetonitrile.

NMR data (solution in $DMSO-d_6$): $\delta(^1H) = 8.51$ (6 H, d, J = 2.5), 6.68 (3 H, t, J = 2.5), 1.65 (4 H, q, J = 7), 1.38 (6 H, t, J = 7); $\delta(^{11}B) = +0.2^*$

($h_{1/2}$ = 600 Hz). Solution in CD_3CN : δ (1H) = 8.13 (6 H, d, J = 2.5), 6.52 (3 H, t, J = 2.5), 1.69 (4 H, q, J = 7.5), 1.42 (6 H, t, J = 7.5); δ (^{11}B) = +0.2 ($h_{1/2}$ = 100).

No effort was made to characterize the hygroscopic tosylate salt. The trifluoromethylsulfonate salt was obtained (in analogous manner as described above but employing ethylboryl ditriflate⁷) as a precipitate from toluene. It was purified by dissolving the crude product in methanol and precipitation with diethyl ether and subsequent recrystallization from acetonitrile. The compound, mp 236-238°C, was obtained in ca. 40% yield.

NMR data (solution in $(CD_3)_2CO$): δ (1H) = 8.45 (6 H, d, J = 2.5), 6.66 (3 H, t, J = 2.5), 1.82 (4 H, q, J = 7.5), 1.49 (6 H, t, J = 7.5). In $DMSO-d_6$: δ (1H) = 8.53, 6.70, 1.67, 1.40. In CD_3CN : δ (1H) = 8.17 (6 H, d, J = 2.5), 6.54 (3 H, t, J = 2.5), 1.70 (4 H, q, J = 7.5), 1.41 (6 H, t, J = 7.5); δ (^{11}B) = +0.3 ($h_{1/2}$ = 100).

$[HB(\mu-pzMe)_3BC_2H_5]^+[PF_6]^-$. A slurry of 5.9 g (20 mmol) of potassium hydrotris(3-methylpyrazol-1-yl)borate⁸ in 100 mL of a 0.2 M solution of ethylboryl ditosylate⁵ in toluene was refluxed with stirring for 3 h. After cooling to room temperature, the solid material was collected and dissolved in 50 mL water. A saturated aqueous solution containing 5.0 g (30 mmol) of ammonium hexafluorophosphate was added with stirring. The desired material precipitated, was collected and washed with water and ether to give 2.3 g (26.1%) of product. After additional washing with a small amount of tetrahydrofuran, it had a mp 225-230°C.

NMR data (solution in CD_3CN): δ (1H) = 7.94 (3 H, d, J = 2.6), 6.30 (3 H, d, J = 2.6), 2.53 (9 H, s), 1.41 (2 H, ill-resolved q), 1.36 (3 H, ill-resolved t); δ (^{11}B) = +0.2 (1 B, s, $h_{1/2}$ = 95 Hz), -8.4 (1 B, d, J = 127).

$[\text{HB}(\mu\text{-pzMe}_2)_3\text{BH}]^+[\text{OTf}]^-$. A solution of 5.1 g (15 mmol) of ethylboryl ditriflate⁷ in 20 mL of toluene was added with stirring to a slurry of 5.05 g (15 mmol) of potassium hydrotris(3,5-dimethylpyrazol-1-yl)borate⁹ in 50 mL of toluene. The mixture was refluxed for 6h. After cooling to room temperature, the insoluble material was collected, washed with 50 mL of water and then with ether to give 3.6 g (52.4% yield) of the crude material. It was purified by dissolving in acetonitrile and precipitation with ethyl acetate, mp 294-298°C (with decomposition).

NMR data (solution in CD_3CN): δ (^1H) = 6.06 (3 H, s), 4.77* (ca. 2 H, s), 2.43 (18 H, s); δ (^{11}B) = -4.1 (d, J = 127).

$(\text{C}_2\text{H}_5)_2\text{B}(\mu\text{-pz})_2\text{B}(\text{pz})_2$.⁴ NMR data (solution in CD_3CN): δ (^1H) = 7.93 (1 H, d, J = 2.2), 7.61 (1 H, d, J = 1.2), 7.44 (1 H, d, J = 2.6), 6.97 (1 H, d, J = 2.1), 6.61 (1 H, t, J = 2.5), 6.26 (1 H, two overlapping d, J = 2.3), 0.4 (5 H, unresolved m); δ (^{11}B) = +3.9* (1 B), +0.3 (1 B). As based on selective decoupling experiments the signals 7.61, 6.97 and 6.26 ppm belong to one pyrazolyl group, the terminal one. Previous NMR data have been reported for solutions in CDCl_3 .¹⁰

$(\text{pz})_2\text{B}(\mu\text{-pz})_2\text{B}(\text{pz})_2$.³ NMR data (solution in CD_3CN): δ (^1H) = 7.57 (2 H, d, J = 2.3), 7.51 (2 H, d, J = 1.5), 6.75 (2 H, d, J = 2.2), 6.65 (1 H, t, J = 2.4), 6.07 (2 H, t, J = 1.7); δ (^{11}B) = +0.7 (s, $h_{1/2}$ = 35 Hz); δ (^{13}C) (proton decoupled) = 143.6, 141.1, 134.9, 109.5, 107.0. Previous NMR data have been reported for solutions in CDCl_3 .¹⁰

Infrared spectrum (KBr pellet): 3100 (sh), 3090 (w), 1770 (vw), 1721 (vw), 1507 (m), 1493 (sh), 1411 (s, br), 1382 (vs), 1342 (m), 1326 (ms), 1291 (vs, br), 1247 (sh), 1233 (s), 1219 (s), 1213 (s), 1202 (s), 1186 (m), 1143 (m), 1095 (s), 1082 (vs), 1060 (m), 1045 (m), 1037 (m), 1023 (m), 971 (vw),

946 (sh), 943 (m), 933 (vw), 918 (m), 889 (sh), 883 (sh), 873 (s), 859 (sh), 851 (sh), 838 (sh), 833 (vs), 816 (m), 811 (s), 786 (s), 782 (sh), 772 (s), 760 (sh), 755 (vs), 673 (sh), 668 (w), 658 (w), 650 (w).

$(C_2H_5)_2B(\mu\text{-pz})_2B(C_6H_5)_2$. A solution of 4.4 g (20 mmol) of diethylboryl triflate⁷ in 25 mL of toluene was added with stirring to a slurry of 6.8 g (20 mmol) of potassium diphenyl-di(1-pyrazolyl)borate¹¹ in 50 mL of toluene. The reaction mixture was refluxed for 4 h. After cooling to room temperature, the mixture was filtered and toluene was evaporated from the clear filtrate to give 7.05 g (95.8%) of the crude product, mp (after recrystallization from cyclohexane) 118-120°C.

NMR data (solution in $CDCl_3$): δ (1H) = 7.66 (2 H, d, $J = 2.4$), 7.39 (2 H, d, $J = 2.4$), 7.20 (6 H, m), 6.94 (4 H, m), 6.40 (2 H, t, $J = 2.4$), 0.43 (10 H, s); δ (^{11}B) = 1.7 ($h_{1/2} = 450$ Hz).

Results and Discussion

The reaction of B-triorganylborexines, $(-BR-O-)_3$ ($R = C_2H_5, C_6H_5$), with pyrazole, Hpz, did not yield the expected pyrazabole $(HO)RB(\mu\text{-pz})_2BR(OH)$. Rather, the reaction stopped after attack of one of the B-O-B bonds of the boroxine ring to give pyrazaboles of the type 2, containing a bridging O-BR-O unit, in very good yield (as based on the employed boroxine).

The structure of the species was readily confirmed by NMR data: The ^{11}B NMR spectra clearly revealed the presence of one three-coordinate and two four-coordinate boron atoms; and 1H and ^{13}C NMR data also confirmed the suggested structure, i.e., the presence of hydrocarbon groups bonded to two types of boron atoms in different environment and also of symmetrically bridging pyrazolyl groups in the correct ratio. In addition, elemental analyses and molecular weight data (obtained by cryoscopy in benzene) confirmed the composition.

In contrast to all previously known pyrazaboles, which can be viewed as intermolecular adducts of two trigonal borane species, compounds of type 2 are formally diboryl oxide derivatives, i.e., $\text{RB}[\text{OBR}(\text{pz})]_2$, but which exist as intramolecular adducts. Remarkably, despite the presence of three-coordinate boron in the structures, the crystalline compounds of type 2 are not moisture-sensitive and are readily handled in air.

At considerably higher temperatures than employed in the above reaction, further interaction was found to occur but was accompanied by extensive ligand rearrangements. This resulted in the formation of pyrazaboles of the type $\text{R}_2\text{B}(\mu\text{-pz})_2\text{BR}_2$ as the only isolated boron-containing species.

Triply-bridged diboron units are also contained in dibora cations of the type $[\text{RB}(\mu\text{-pz})_3\text{BR}]^+$. Only two examples of such species have so far been described in the literature. The first one, $[\text{C}_2\text{H}_5\text{B}(\mu\text{-pz})_3\text{BC}_2\text{H}_5]^+$, was obtained as a minor product on interaction of ethylboryl ditosylate, $\text{C}_2\text{H}_5\text{B}(\text{OTs})_2$ ($\text{OTs} = \text{O}_3\text{SC}_6\text{H}_4\text{-4-CH}_3$), with pz^- ion and was isolated as the hexafluorophosphate salt; no experimental details were given.⁵ The structure of the species was, however, confirmed by ^1H NMR⁵ and X-ray diffraction¹² data. The second example, $[\text{HB}(\mu\text{-pzMe}_2)_3\text{BH}]^+$ ($\text{HpzMe}_2 = 3,5\text{-dimethylpyrazole}$), was accidentally obtained in low yield when $\text{K}[\text{HB}(\text{pzMe}_2)_3]$ was reacted with MCl_5 ($\text{M} = \text{Nb, Ta}$). Although the process of formation of the cation is not well understood, its structure was again confirmed by NMR and X-ray crystallographic data.⁶

When potassium pyrazolide, Kpz , was reacted with $\text{C}_2\text{H}_5\text{BX}_2$ ($\text{X} = \text{OTs}$ or $\text{O}_3\text{SCF}_3 = \text{OTf}$) in 3:2 molar ratio, the desired cation $[\text{C}_2\text{H}_5\text{B}(\mu\text{-pz})_3\text{BC}_2\text{H}_5]^+$ was obtained in about 20 ($\text{X} = \text{OTs}$) or 40 ($\text{X} = \text{OTf}$) % yield, respectively. The tosylate salt of the cited cation is extremely hygroscopic and it is best to

convert it immediately to the hexafluorophosphate salt. The triflate salt is only slightly soluble in water but readily dissolves in methanol or acetone. Remarkably, no defined boron-containing product could be obtained from KpzMe_2 and $\text{C}_2\text{H}_5\text{BX}_2$ under analogous reaction conditions.

In another set of experiments, $[\text{RB}(\text{pz})_3]^-$ ions ($\text{R} = \text{H}$ or pz) were reacted with $\text{C}_2\text{H}_5\text{BX}_2$. Both $[\text{HB}(\text{pz})_3]^-$ and $[\text{B}(\text{pz})_4]^-$ gave only the cation $[\text{C}_2\text{H}_5\text{B}(\mu\text{-pz})_3\text{BC}_2\text{H}_5]^-$ and no species with unsymmetrical substitution at the boron atoms could be obtained. In the reaction of $[\text{HB}(\text{pz})_3]^-$, the yield of the cation was comparable to the one obtained in the preparation originating from the pz^- ion; and for $[\text{B}(\text{pz})_4]^-$, the yield was only about 5%. No other defined boron-containing products could be identified as products in these reactions. On the other hand, when stereochemically pure $[\text{HB}(\text{pzMe})_3]^-$ ($\text{HpzMe} = 3\text{-methylpyrazole}$) was reacted with $\text{C}_2\text{H}_5\text{BX}_2$, the desired unsymmetrical cation $[\text{HB}(\mu\text{-pzMe})_3\text{BC}_2\text{H}_5]^+$ was obtained. NMR spectral data of the species clearly confirm its structure and also the formation of only one isomer. This latter observation tends to suggest that the ion $[\text{HB}(\text{pzMe}_3)]^-$ reacts as such and no intermediate cleavage of a boron-pyrazolyl bond is involved. Surprisingly, $[\text{HB}(\text{pzMe}_2)_3]^-$ reacted with $\text{C}_2\text{H}_5\text{BX}_2$ to form the species $[\text{HB}(\mu\text{-pzMe}_2)_3\text{BH}]^+$.

The foregoing observations suggest a directive influence of the (pyrazole-)methyl groups with respect to the resulting product but do not explain the differing rearrangements of the boron substituents. Presumably, in the above case of reacting the $[\text{HB}(\text{pz})_3]^-$ and $[\text{B}(\text{pz})_4]^-$ ions, an unsymmetrically B-substituted ion, $[\text{RB}(\mu\text{-pz})_3\text{BC}_2\text{H}_5]^+$ ($\text{R} = \text{pz}$ or H), is formed initially but this is followed rapidly by displacement of the boron-bonded R by an ethyl group. On the other hand, the results of the reaction of $\text{K}[\text{HB}(\text{pzMe}_2)_3]$ with $\text{C}_2\text{H}_5\text{BX}_2$ illustrate that a reverse ligand exchange, i.e., displacement of ethyl by H , is also possible.

Unusual ligand redistribution reactions have also been observed in other instances. For example, the reaction of $K[(C_6H_5)_2B(pz)_2]$ with $(C_2H_5)_2BOTf$ readily gave the desired pyrazabole $(C_6H_5)_2B(\mu-pz)_2B(C_2H_5)_2$. This reaction was found to proceed much more smoothly than the reaction of $[B(pz)_4]^-$ with $(C_2H_5)_2BOTs$ to yield the pyrazabole $(pz)_2B(\mu-pz)_2B(C_2H_5)_2$.⁴ As a matter of fact, this latter reaction is not easily duplicated but most often yields the symmetrical pyrazabole $R_2B(\mu-pz)_2BR_2$ with $R = C_2H_5$ under apparently identical conditions. Thus, the present study illustrates that the ligand exchange reactions are not yet well understood and often are unpredictable.

Finally, it is worth mentioning that a fairly strong solvent effect has been noticed not only for terminal but also bridging pz groups of pyrazaboles when the 1H NMR spectra are recorded. For example, the terminal-pz 1H signals of $(pz)_2B(\mu-pz)_2B(C_2H_5)_2$ were observed at $\delta = 7.73/6.94/6.26$ in $CDCl_3$,⁹ 7.61/6.97/6.26 in CD_3CN ; and the bridging-pz 1H signals were found at 7.76/7.46/6.52 in $CDCl_3$ ⁹ but at 7.91/7.44/6.61 in CD_3CN . The corresponding values for $(pz)_2B(\mu-pz)_2B(pz)_2$ are δ (in $CDCl_3$) = 7.70/6.81/6.1 (terminal pz) and 7.67/6.70 (bridging pz),⁹ but δ (in CD_3CN) = 7.57/6.75/6.07 and 7.51/6.65, respectively. This may impair the assignments of 1H NMR signals of pyrazaboles by correlation if different solvents are employed.

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